

NOVEL LASER GAIN AND TIME-RESOLVED FTIR STUDIES  
OF PHOTOCHEMISTRY

STEPHEN R. LEONE†

Joint Institute for Laboratory Astrophysics, National Institute of Standards and Technology and University of Colorado, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0440

## ABSTRACT

Several novel techniques are discussed which can be used to explore laboratory photochemical processes and kinetics relevant to planetary atmospheres; these include time-resolved laser gain-versus-absorption spectroscopy and time-resolved Fourier transform infrared (FTIR) emission studies. The laser gain-versus-absorption method employs tunable diode and F-center lasers to determine the yields of excited photofragments and their kinetics. The time-resolved FTIR technique synchronizes the sweep of a commercial FTIR with a pulsed source of light to obtain emission spectra of novel transient species in the infrared. These methods are presently being employed to investigate molecular photodissociation, the yields of excited states of fragments, their subsequent reaction kinetics, Doppler velocity distributions, and velocity-changing collisions of translationally fast atoms. Such techniques may be employed in future investigations of planetary atmospheres, for example to study polycyclic aromatic hydrocarbons related to cometary emissions, to analyze acetylene decomposition products and reactions, and to determine spectral features in the near infrared and infrared wavelength regions for planetary molecules and clusters.

## INTRODUCTION

The atmospheres of many planets other than the Earth can involve extreme temperatures and pressures, and they contain many highly chemically reactive constituents as well. For example, several planets exist in a strongly reducing atmosphere, composed largely of methane and other hydrocarbon species at high pressures near the surface and low outer temperatures.<sup>1</sup> Thus the typical mixtures of gases are not only unfamiliar, but their spectral signatures as we might

know them are strongly perturbed by the unusual conditions of temperature and pressure. The molecular species are also undoubtedly in a state of flux, undergoing dramatic transformations because of photochemistry and solar heating. As a result, there is a definite need to develop techniques to study the kinds of planetary atmosphere species which may only be formed under such unusual conditions. Recording their molecular spectra and studying their distinctive photochemistry will be of great importance.

A wide variety of powerful spectroscopic probes have been developed in the past several years, which have provided a means for detection of novel transient species and for probing their kinetics. These include methods such as laser-induced fluorescence in the visible and ultraviolet,<sup>2</sup> laser multiphoton ionization,<sup>3</sup> intracavity laser absorption,<sup>4</sup> and transient absorption/gain probing with lasers.<sup>5</sup>

Of special interest in this article are two methods applicable to the spectral features of molecular species in the infrared and near infrared. These are time-resolved Fourier transform infrared (FTIR) emission spectroscopy<sup>6</sup> and tunable infrared laser gain-versus-absorption spectroscopy.<sup>5,7,8</sup> These methods rely heavily on lasers, both for the initial preparation of transient species, and in the case of the laser gain/absorption method, also for the transient detection. Lasers are extremely useful for the preparation of large number densities of transient and reactive species. With the time-resolved FTIR method, it is possible to form a variety of excited molecular species and to study the infrared spectral details of the emitting states. With the laser gain-versus-absorption technique, we can study quantum yields for the formation of excited states and the kinetics of radical reactions.

Work is ongoing in our laboratory to develop a variety of these infrared and near infrared techniques and to achieve advanced capabilities in their application to important problems. The methods are applicable to a number of challenges related to planetary atmospheres, including infrared cometary emissions which may be due to large molecules, such as polycyclic aromatic hydrocarbons,<sup>9</sup> and acetylene chemistry and photochemistry.<sup>10</sup> In the remainder of this paper, the general experimental setups for these two types of methods will be described, and a few examples will be given, for each method, of the kinds of problems that have already been addressed in our laboratory. We close with a brief introduction to several subjects related to planetary atmospheres that might be studied by these techniques.

## TIME-RESOLVED FTIR EMISSION METHOD

Commercial Fourier transform infrared (FTIR) instruments provide a powerful means to detect and study a wide range of molecular species in the infrared and near infrared. A novel

adaptation<sup>6</sup> takes advantage of the sensitive emission capabilities in the infrared by using a laser to prepare photofragments or other excited species and then imaging their infrared emission through the FTIR. By synchronization of the timing of a pulsed laser with the sweep of the mirror in the FTIR, complete time histories of the spectral information can be obtained of transient radical species, chemically reacting systems, and energy transfer processes. Such a method may be well suited to studies of unusual species and conditions typical of planetary atmospheres. In some cases, direct laboratory spectral information may be compared to emissions observed by planetary and cometary probes.

Figure 1 shows a schematic of a time-resolved FTIR system in use in our laboratory.<sup>11,12</sup> A pulsed high repetition rate excimer laser (200-400 Hz) is paired with a commercial high resolution FTIR (0.02 cm<sup>-1</sup>), which is operated in the emission mode. The laser produces photofragments in either a low pressure chamber or in a high pressure flow cell reactor, and emission is collected into the interferometer from the infrared emitting species. The timing of the pulsed laser is synchronized to the sweep of the mirror in the FTIR through the reference fringes of the He:Ne laser. Data may be collected at either a single time or multiple times after the laser pulse (Fig. 2). If signals are acquired at multiple times, then on the next sweep of the mirror, the timing

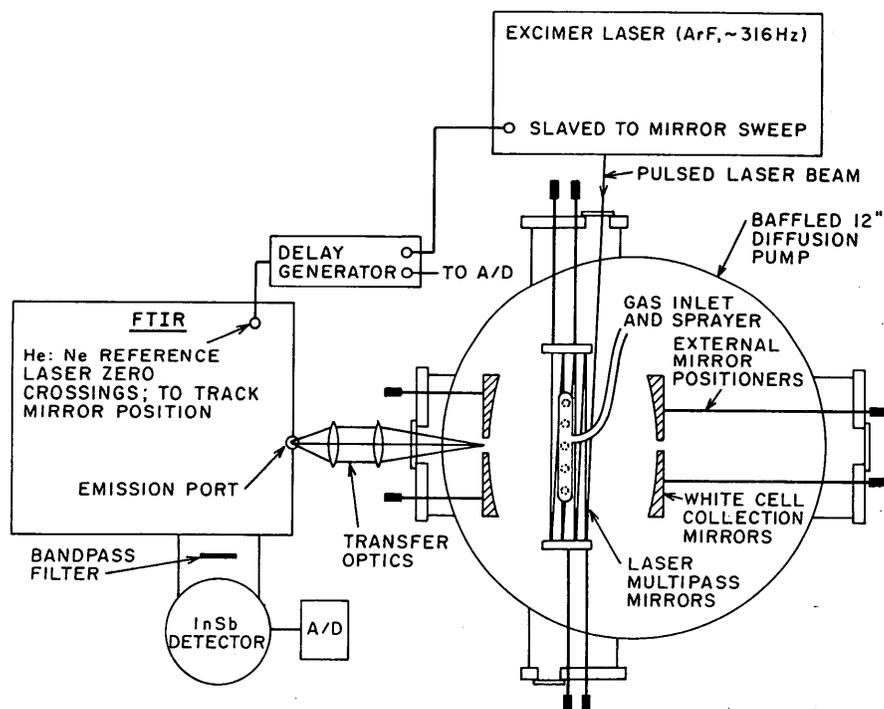


Fig. 1. Experimental apparatus for time-resolved FTIR emission experiments initiated by laser photodissociation.

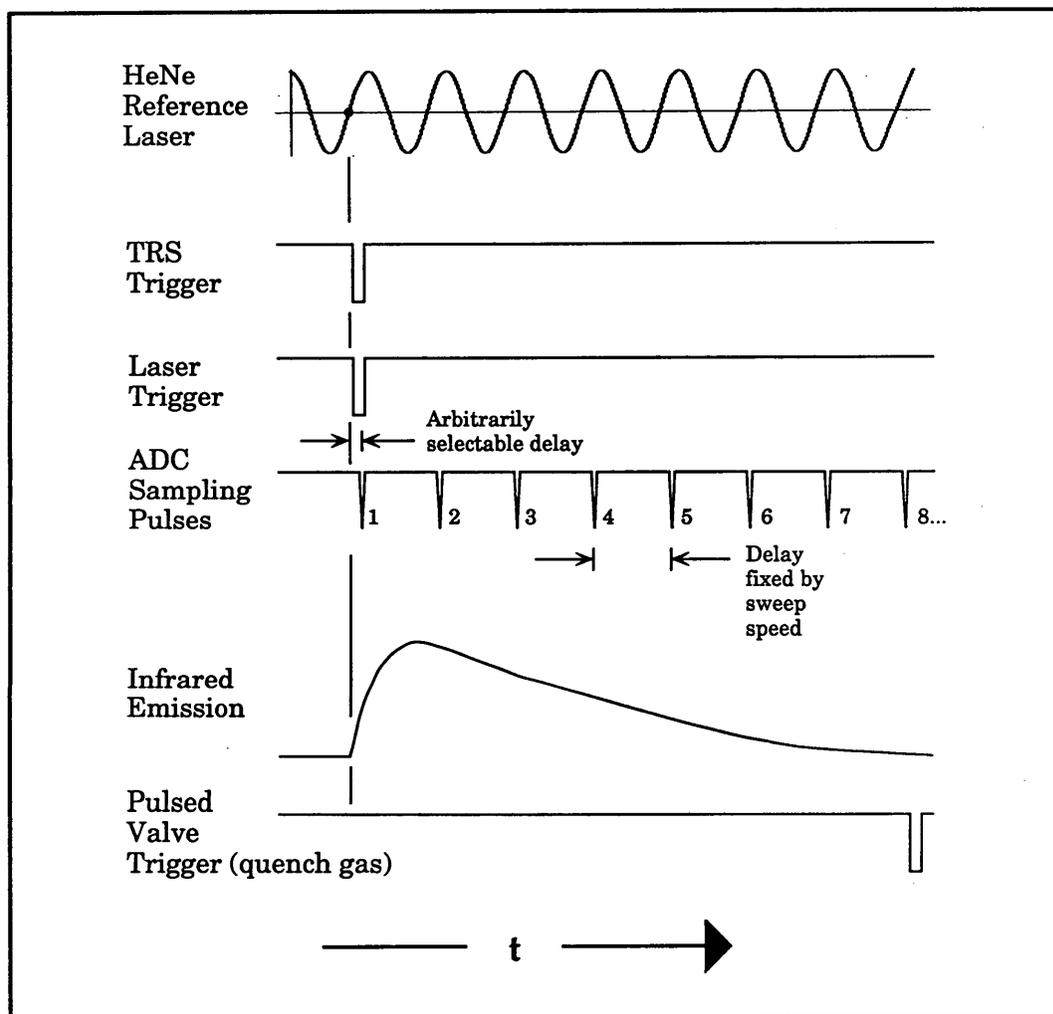


Fig. 2. Timing diagram for time resolved FTIR emission experiment, showing 8 time samples after each laser pulse.

of the acquisition is adjusted such that the next laser pulse is incremented in order to obtain data at each time delay for every mirror displacement.

Infrared emission has the advantage that relatively low numbers of excited species are readily detectable ( $10^9$ - $10^{11}$ ), in contrast to absorption, where long pathlengths and large volumes are often necessary. Thus, small numbers of highly exotic species may be prepared and observed under desired conditions through their emission. The pulsed laser may also be replaced by a cw laser, flashlamp, or other excitation source, in order to obtain high average emissions, and the cells may be heated or cooled or operated under high pressures to simulate planetary atmosphere conditions.

## Acetylene Photochemistry

The photodissociation of acetylene (HCCH) at 193 nm in the ultraviolet has an important radical-forming channel, CCH+H; the CCH radical, which may be excited both vibrationally and in a low-lying electronically excited state ( $\tilde{A}^2\Pi$ ) has been observed in infrared emission following the photodissociation of acetylene with the time-resolved FTIR method.<sup>13</sup> Figure 3 shows a survey spectrum of the CCH radical emission, which required only about 1 hour to acquire with the FTIR. While the CCH radical has been studied in line-by-line detail with transient laser absorption probing,<sup>14</sup> the power of the FTIR method to obtain rapid information about the broad spectral content of unusual species is readily apparent. Not only are infrared bands of vibrationally excited states of CCH expected, but the strongest infrared and near infrared emission features of this radical are composed of bands involving the ( $\tilde{A}^2\Pi$ ) electronically excited state, which occur at unanticipated wavelengths. In terms of planetary photochemistry and spectral signatures, the potential capability of the broad spectral coverage of the FTIR method may be advantageous for laboratory studies.

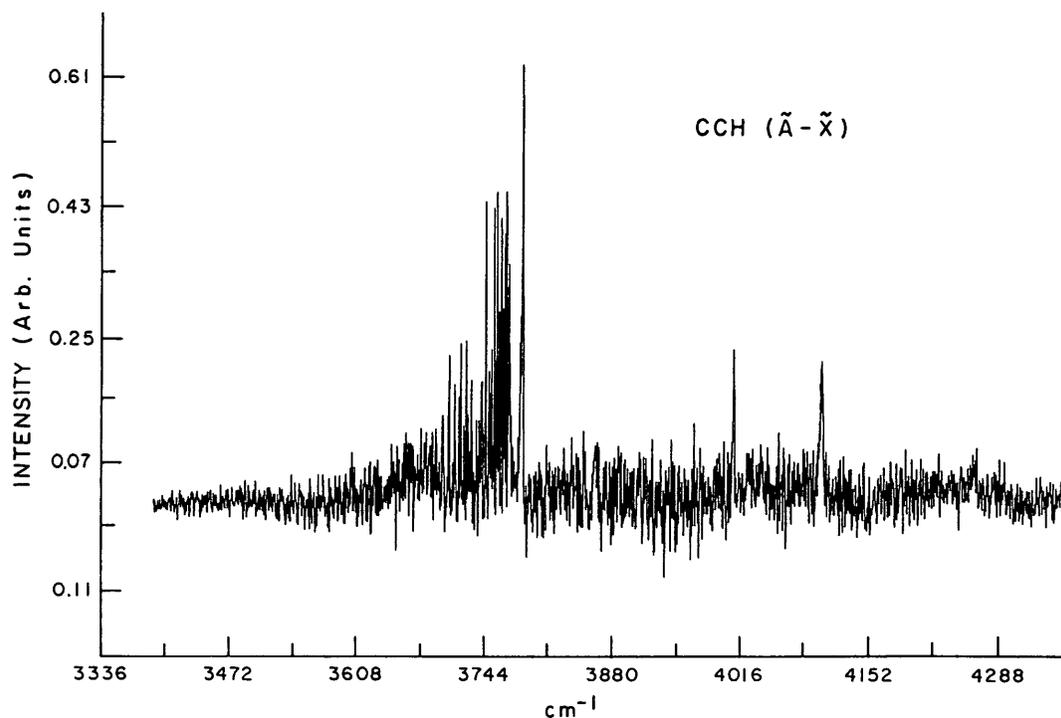


Fig. 3. Infrared emission spectrum of CCH taken with the FTIR at 0.6 cm<sup>-1</sup> resolution at a time of 7  $\mu$ s after the photolysis of acetylene.

In work carried out in our laboratory, the vibrational band intensities produced by the UV photolysis of acetylene were obtained. In addition, an intriguing problem arises in the primary photochemistry of acetylene concerning the rotational excitation of the CCH radical that is caused by the momentum transfer of the departing H atom.<sup>13</sup> The rotational excitation of the CCH radical is found, surprisingly, to be colder than the initial excitation in the parent acetylene. This is an unanticipated result, because the momentum transfer from the departing H atom might typically be expected to produce additional rotational excitation in the radical. The rotational dynamics are modeled in terms of both a trans-bent and linear transition state. It is found that in the trans-bent configuration the constraint of the available energy in the photodissociation may cause a constraint on the allowed angular momentum states, resulting in a "cooling" of the radical product.<sup>13</sup>

### Acetone Photodissociation

The photochemistry of acetone also offers several intriguing aspects of study.<sup>12</sup> The 193 nm photodissociation produces a three-body dissociation pathway to form two methyl radicals ( $\text{CH}_3$ ) and carbon monoxide (CO). The broad spectral features of the emission from this dissociation were obtained initially with low resolution infrared circular variable filters (CVF).<sup>15</sup> Emission is observed from CH stretching regions and from the vibration-rotation excitation of the CO fragment. While such low resolution spectra are useful to gain a coarse perspective on the infrared emitting species, the much higher resolution of the FTIR method allows detailed state-resolved information to be obtained (Fig. 4). From the high resolution spectra taken at low pressures, it is found that the CO is born with very high excitation in both rotation and vibration. The high rotational excitation can only be explained if the three body dissociation occurs by a nonsymmetric break-up.<sup>12</sup>

Figure 5 shows a portion of the FTIR spectrum of the methyl radical antisymmetric stretching region, observed in the photolysis of acetone.<sup>16</sup> All of the lines are assignable to methyl radical features, based on the known spectroscopy. An intriguing problem which is yet to be resolved concerns the origin of this methyl radical infrared emission. Laser multiphoton ionization detection of the methyl radical following the photodissociation of acetone has not observed the antisymmetric stretch excitation.<sup>17</sup> Either the radical is born with excitation in other modes, which is then transferred to the antisymmetric stretch vibration and emits in the infrared, or the multiphoton ionization detection is insensitive to the antisymmetric stretch because of unusual Franck-Condon factors or some other spectroscopic subtlety.

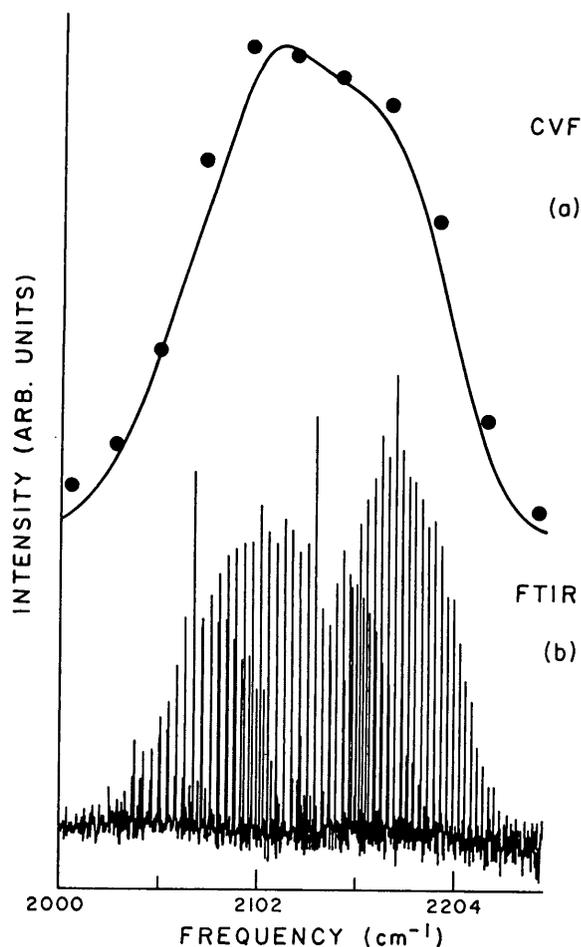


Fig. 4. Comparison of CO emission spectra following acetone photodissociation taken with (a) a low resolution circular variable filter (CVF) and (b) the high resolution FTIR.

### Radical-Radical Reactions

The FTIR method is proving to be a powerful tool not only to investigate primary photochemical events, but to study potentially novel, subsequent reaction chemistry. In a new series of experiments, a high density of Cl atoms is produced by excimer laser photolysis of Cl<sub>2</sub> in the presence of a low density of ethane. A reaction between Cl and C<sub>2</sub>H<sub>6</sub> occurs, producing a quantitative yield of ethyl radicals, C<sub>2</sub>H<sub>5</sub>. Since the Cl atoms are initially in excess compared to the ethane, then a rapid reaction can occur between the remaining Cl atoms and the ethyl radicals, C<sub>2</sub>H<sub>5</sub>, to form HCl and ethylene, C<sub>2</sub>H<sub>4</sub>. The signature of the radical-radical reaction is the formation of highly vibrationally excited HCl, which cannot occur for the reactions of the atoms with stable molecules, as ascertained from the known thermochemistry. Highly vibrationally excited HCl has now been observed in an initial series of experiments,<sup>16</sup> suggesting that intriguing new investigations will be possible to study systems in a state of high energization, such as radical-radical chemistry. Such reactions are likely to be much more rapid and more exothermic than

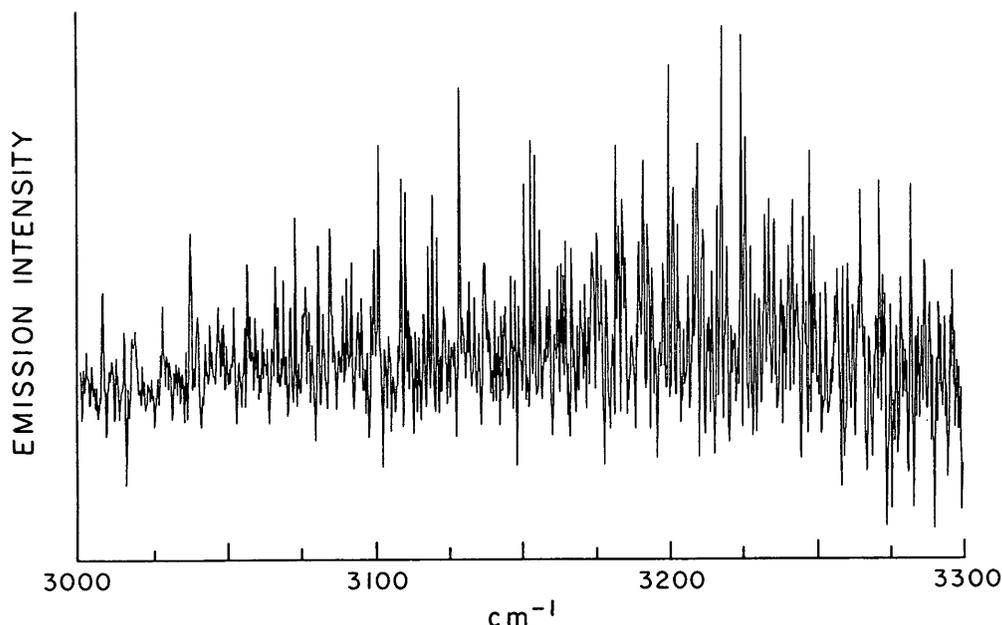


Fig. 5. Methyl radical antisymmetric stretch emission spectrum following the photolysis of acetone.

traditional abstraction reactions with stable molecules, and may be sources of strong infrared emission and highly excited products.

#### TRANSIENT GAIN-VERSUS-ABSORPTION LASER KINETICS METHOD

While the FTIR method is an excellent tool for surveys of emitting systems and detailed investigations of state distributions in photochemistry, other methods provide accurate complementary information on such questions as kinetics or quantum yields of formation for excited or ground state species. One such method is the time-resolved laser gain-versus-absorption technique, which has also been used extensively for laser spectroscopic measurements. In our laboratory, the laser gain-versus-absorption method was initially developed to obtain some of the most accurate values for quantum yields of formation. The method was applied to the excited  $\text{Br}^*(2P_{1/2})$  and  $\text{I}^*(2P_{1/2})$  states of the halogen atoms using a tunable infrared F-center laser and a tunable room temperature diode laser as the probes, respectively.

Figure 6 illustrates the typical setup for the transient gain-versus-absorption kinetics determinations.<sup>5,18,19</sup> A pulsed photolysis laser forms a population of ground and excited halogen atoms, in this case I and  $\text{I}^*$ . A tunable diode laser, which is set to probe the transition between the

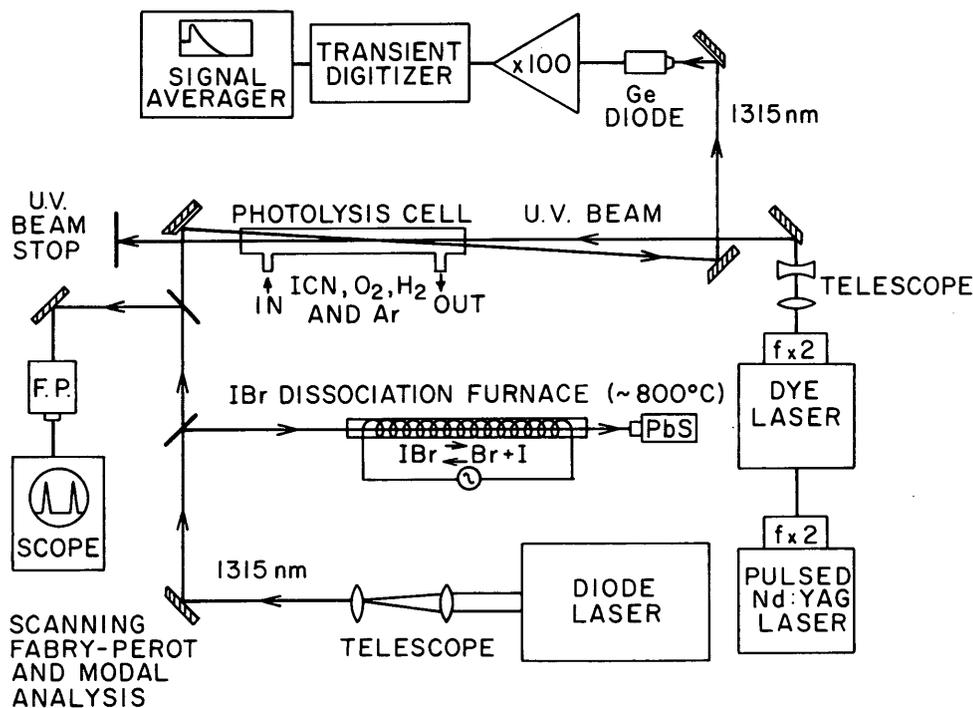


Fig. 6 . Laser gain-versus-absorption apparatus using a diode laser to study I\* quantum yields. The heated IBr cell is for tuning the diode laser to the I atom transition.

two states at 1315 nm, is propagated collinearly in order to measure the transient gain or absorption of the atomic population. If the population of atoms contains more excited states than ground states, when the factor of the differing degeneracies is taken into account, then laser gain will be observed initially (shown in Fig. 7 for ICN photolysis). If the ground state population dominates, then an initial absorption is observed. At a later time, when all the excited states are relaxed by a suitable quenching species, the relative population of the total number of atoms formed in both states is determined. From the initial and final measurements, a highly accurate relative quantum yield is determined. If, in addition, it is known that the molecules fragment to the desired atom with a certain yield, then absolute quantum yields are obtained.

### Quantum Yield Determinations

For the case of I\*, the degeneracy of the upper state is 2 and for the ground state, 4. Thus, a very simple expression may be derived under the conditions of the experiment, namely that the quantum yield of formation of the I\* state is given by:<sup>5,18,19</sup>

$$\Phi_{I^*} = (1/3) (S_i/S_f + 1). \quad (1)$$

Thus, if the initial and final amplitudes of the laser gain-versus-absorption signal are measured, the quantum yield is immediately obtained. By making determinations as a function of wavelength, the quantum yield is immediately obtained over various spectral bands, as shown in Fig. 8 for the case of the ultraviolet photodissociation of ICN. In our work on the halogen atom quantum yields, typical accuracies of  $\pm 2\%$  are achieved. This improves on the accuracy of previous determinations by one order of magnitude. The method may be extended to obtain quantum yields of other excited states of atoms.

The laser gain-versus-absorption method also allows accurate quenching rate constants and kinetic parameters to be determined from the time behavior of the signals. Tunable diode lasers operating throughout the entire infrared spectral region have now been employed in this method, used in various laboratories.

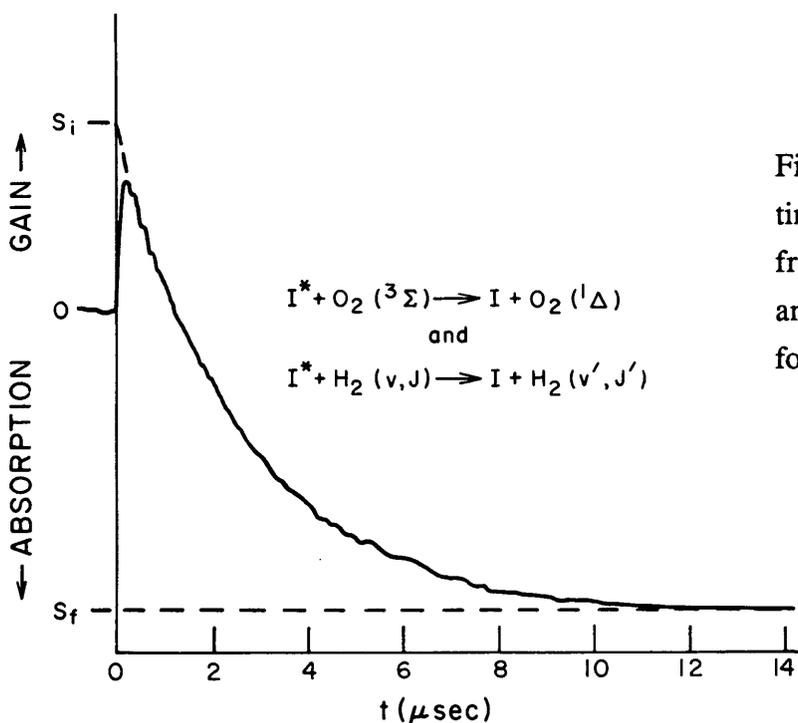


Fig. 7. Laser gain-versus-absorption time transient from ICN dissociation; from the initial and final signal amplitudes, a quantum yield for  $I^*$  formation is obtained.

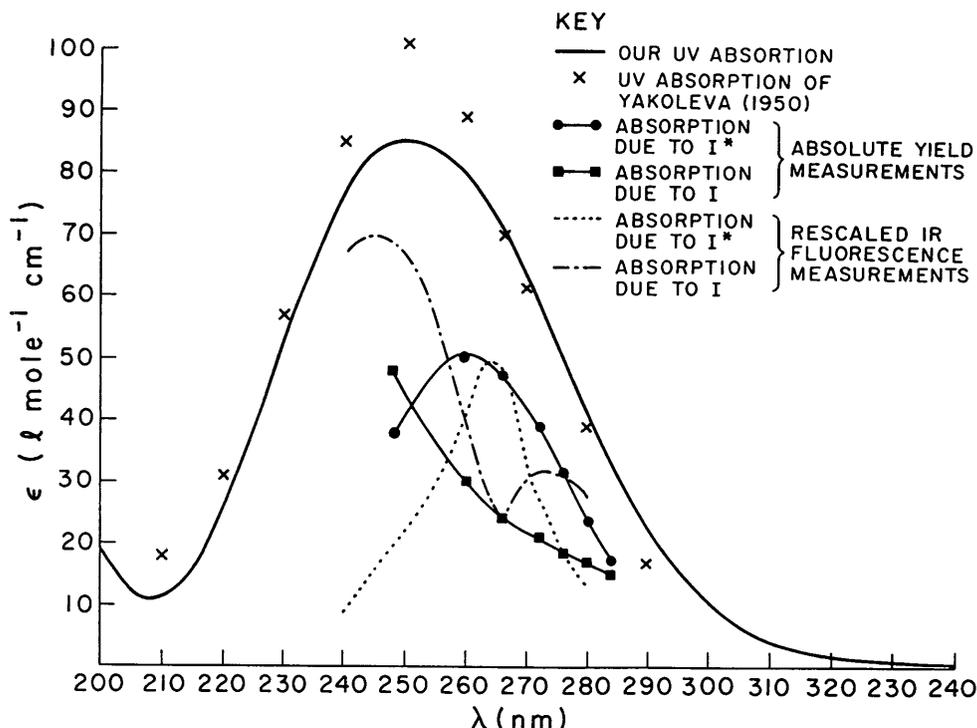


Fig. 8. Spectrally-resolved I\* quantum yields as a function of dissociating wavelength. For the details of the legend, see Ref. 19.

## POTENTIAL APPLICATIONS TO PLANETARY ATMOSPHERES

The time-resolved FTIR emission technique and laser gain-versus-absorption method provide an excellent basis for further studies of exotic species related to laboratory investigations of planetary atmospheres.<sup>20</sup> Future work may utilize the FTIR to study the infrared emission spectra of polycyclic aromatic hydrocarbons (PAH's) excited by ultraviolet light, in order to determine their role in cometary emissions. Additional species related to the PAH's are the classes of hydrogenated amorphous carbon and vitrinite coal particles, which are characterized by higher oxygen contents.<sup>9,21</sup> Acetylene photochemistry and reactions may also be investigated in a broad way by these methods, as well as individual atom-radical reactions which may play an important role in the planetary atmospheres. One example is the reaction of N atoms with CH<sub>3</sub> radicals, which may play a role in the atmosphere of Titan.<sup>22</sup> The FTIR method would allow the identification of product species and emitting states, in order to determine the role of this reaction in the possible formation of HCN in the atmosphere of this moon. Use of the laser gain/absorption technique will provide refined kinetic determinations and quantum yields of novel species.

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